Structural precursor to adsorbate-induced reconstruction: C on Ni(100)

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The local structure around adsorbed carbon atoms on Ni(100) has been determined at low coverage as well as in the 0.5 monolayer $(2 \times 2)p4g$ ''clock'' reconstruction by scanned energy mode photoelectron diffraction. At low coverage, there is no radial strain of the Ni atoms surrounding the adsorbed carbon, contrary to previous suggestions. None of the C-Ni near-neighbor distances are changed by reconstruction, but the Ni-Ni nearest-neighbor distance in the top layer increases significantly, showing that the adsorbate-induced compressive stress is associated with Ni-Ni, rather than Ni-C, repulsion. [S0163-1829(99)01739-7]

It is now widely recognized that the structure of the outermost atomic layers of solids are generally modified in the presence of adsorbates, although it is only in a limited number of systems that true adsorbate-induced reconstruction occurs, leading to significant substrate atom movements parallel to the surface or to a change in the atomic density of the outermost layers. One of the best-known examples of this situation is the influence of C adsorption on Ni(100) in which, at a coverage of 0.5 ML (monolayers) a $(2 \times 2)p4g$ phase is formed which has been shown to involve a ''clock'' reconstruction of the outermost Ni layer;[1–4] the top-layer Ni atoms are displaced parallel to the surface, partly by alternate clockwise and counter-clockwise rotations about the C atoms in such a way that the hollow sites occupied by the C atoms are enlarged [Fig. 1(b)]. The detailed atomic coordinates in this structure are now rather well established by a variety of techniques. However, debate has continued concerning the origin of this adsorbate-induced reconstruction; relief of adsorbate-induced compressive surface stress has been implicated,[5] but there have also been suggestions that attraction of the C atoms to the underlying second-layer Ni atom is crucial.[6]

In a scanning tunnelling microscopy (STM) investigation of this system, Klink *et al.*[6] saw direct evidence for the lateral distortions of the $(2 \times 2)p4g$ phase described above, but also studied the surface at low coverage. Under these circumstances they concluded that the C atoms adsorb in hollow sites without inducing a local clock reconstruction, but induce a lateral (radial) outward relaxation of the nearest-neighbor top-layer Ni atoms [Fig. 1(a)]; this local strain was interpreted as a signature of Ni-C near-neighbor repulsion taken to define the mechanism of the reconstruction. This type of quantitative interpretation of STM images of adsorbate systems in terms of nuclear coordinates is, however, fraught with difficulties, and while the main character of the disorder-order transition with increasing coverage is shown clearly by this work, quantitative details of the local structure still require a true structural probe. Only with this informa-

tion can one draw reliable conclusions about strain implications of surface stress changes. Here, we present the results of such a study using the technique of scanned energy mode photoelectron diffraction (PhD), a method that allows the local geometry around an adsorbate atoms to be determined quantitatively without any need for long-range order.[7] The associated problem of studying the C $1s$ photoemission signal (which has a low-associated cross-section) at low-adsorbate coverage has been overcome through the use of undulator radiation from the new third-generation synchrotron radiation advanced light source (ALS). Contrary to the prior interpretation of the STM images, we find that while the C atoms at low coverage do occupy hollow adsorption sites, there is no significant lateral relaxation of the surrounding Ni atoms, although their layer spacing is modified as also suggested by the STM data. By studying both the low coverage and 0.5 ML $(2 \times 2)p4g$ phases, we obtain detailed geometrical parameters and show that the distortions induced in the reconstruction actually conserve the C-Ni nearest-neighbor distances in both the outermost two layers, but the
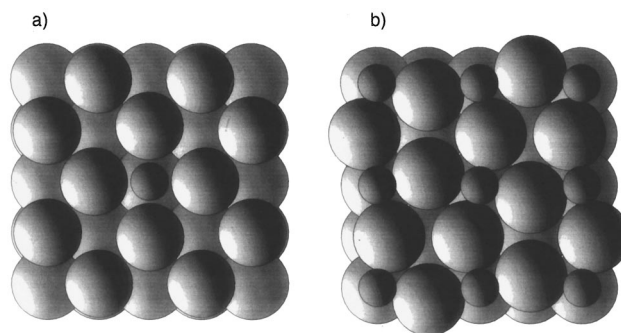

FIG. 1. Schematic plan views of the Ni(100) surface in the presence of (a) an isolated C adsorbate and (b) the $(2 \times 2)p4g$ reconstruction produced by 0.5 ML of C. The open and shaded large circles represent outer and second-layer Ni atoms, the filled smaller circles show C atom sites. The magnitude of the lateral distortions of the outermost Ni atoms are discussed in the text.

Ni-Ni distances in the top layer change significantly. Our results highlight the importance of precise and quantitative surface structural studies; the absence of local Ni-C strain is superficially far less interesting than the spurious conclusions drawn from the STM images, but by identifying the correct nearest-neighbor distances we can isolate the true structural fingerprint of the reconstruction.

In the PhD technique[7] the photoemission signal emitted in a specified direction from an adsorbate core level is measured as a function of photon (and thus photoelectron) energy. This signal comprises a coherent sum of the directly emitted photoelectron wave field and components of the same wave field elastically scattered from atoms surrounding the emitter; as the photoelectron energy, and thus the photoelectron wavelength is varied, the contributions of specific scattering paths pass through constructive and destructive interference conditions and thus, lead to modulations in intensity. A full quantitative structure analysis is effected through the use of full multiple scattering simulations for a series of trial structures, but we have also shown that as a preliminary to this process a good indication of the local geometry can be obtained by a direct inversion of the experimental PhD spectra recorded in several different directions using the so-called projection method.[8,9] Underlying this method is the observation that when the emission direction is such as to place a near-neighbor substrate atom directly behind the emitter, in the favored 180° backscattering geometry, the PhD spectral modulations are dominated by the contributions from this one scattering path.

The experiments were conducted at beamline 7.0.1 of the ALS (Ref. 10) and the Ni(100) crystal was prepared by the usual combination of Laue x-ray orientation, spark-machining, polishing and *in situ* argon-ion bombardment and annealing. The good surface long-range order and cleanness were established by *in situ* low energy electron diffraction (LEED) observations and the use of soft x-ray (synchrotron radiation) photoelectron energy spectra. Carbon deposition on the surface was effected by exposure to ethylene at a pressure of 10^{-9} to 5×10^{-8} mbar and a sample temperature of 520 K [a saturation exposure of 5 L for the (2×2) phase and 0.08 L for the low-coverage phase]. The C 1s photoemission spectra were recorded using a Perkin-Elmer Omni IV hemispherical analyzer of mean radius 137 mm fitted at a fixed angle of 60° to the incident photons. PhD spectra were obtained from a succession of such photoelectron energy spectra recorded at photon energy increments chosen to correspond to constant increments in the photoelectron wave vector through the kinetic energy range of 90 to 430 eV, at polar emission angles from 0° (along the surface normal) to 80° in each of the two principle azimuths, $\langle 100 \rangle$ and $\langle 110 \rangle$. The two surface phases studied were that leading to the $(2 \times 2)p4g$ LEED pattern, which saturates at a carbon coverage of 0.5 ML, and a (1×1) (disordered) phase at a coverage of 0.15 ML.

Application of the projection method[8,9] to these data leads to a three-dimensional map of a function, C, whose amplitude is largest at positions most likely to correspond to the positions of substrate scatterer atoms relative to the emitter. Figure 2 shows sections parallel to the surface and just below the emitter for the low-coverage phase at a spacing perpendicular to the surface chosen to intersect the most intense
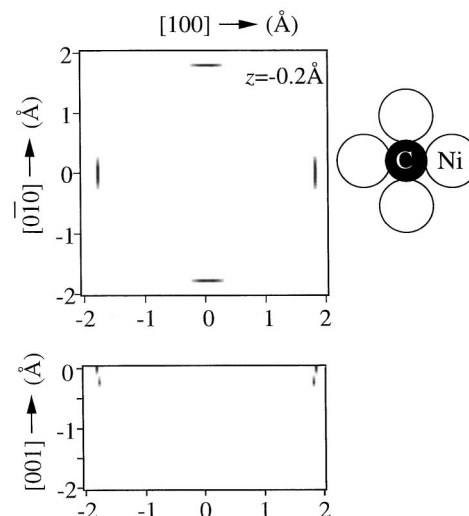

FIG. 2. Results of the projection method of direct data inversion applied to C 1s PhD data from C adsorbed on Ni(100) at a coverage of 0.15 ML, compared with a structural model of the local geometry. The projection method data are shown in the form of gray-scale maps parallel to the surface but just below the C emitter atom as described in the text, the darkest features corresponding to positions most likely to be occupied by a substrate scatterer atom.

features. Also shown in Fig. 2, for comparison, is the implied local structure with the C emitter atom occupying a simple undistorted hollow site on the Ni(100) surface. A clear signature of these top-layer nearest-neighbors, and their rotation out of the $\langle 100 \rangle$ azimuth in the higher coverage clock reconstruction is seen very directly in the PhD spectra recorded at grazing emission angles, and especially at 80° emission in the $\langle 100 \rangle$ azimuth corresponding to the C-Ni nearest-neighbor direction in the outermost Ni atom layer (Fig. 3). In the unreconstructed low-coverage phase extremely intense ($> \pm 60\%$) modulations are seen with long periodicity corresponding to the single-dominant back scatterer. In the $(2 \times 2)p4g$ phase the modulations are weaker and show contributions from other (longer) scatterer paths, as the Ni near neighbors are now displaced away from the optimum backscattering geometry. Notice, by contrast, that the near-normal emission spectra, dominated by backscattering from the second layer Ni atom below the adsorbed C atom, are strongly modulated in both phases.

These results simply confirm the known structure of the $(2 \times 2)p4g$ phase and show that the interpretation of the STM images of the low-coverage phase in terms of essentially unreconstructed hollow site occupation was correct. A full analysis of the PhD data, however, allows us to test the more quantitative conclusions of the STM study concerning the local substrate distortion at the hollow site in the low-coverage phase. The details of the multiple scattering calculations[11] and the structural optimization based on a reliability factor[12] have been discussed elsewhere and applied successfully to a large number of adsorption structures.[7] Table I summarizes the results of this quantitative structure determination for the two Ni(100)/C phases based on our PhD data, and Fig. 3 shows a comparison of the experimental and best-fit theoretical PhD spectra measured in six different emission directions that were optimized in both analyses. The structural parameter values for the long-range
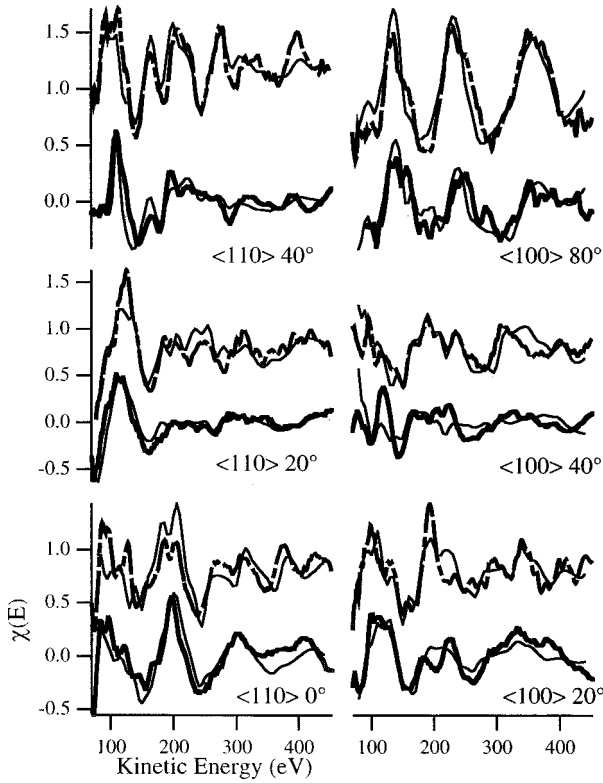
FIG. 3. Comparison of experimental (bold curves) C $1s$ PhD data recorded in six different emission azimuths and polar angles from C adsorbed on Ni(100) at coverages of 0.15 ML (dashed lines) and 0.5 ML (full lines) with the best-fit theoretical simulations (thin lines).

ordered $(2 \times 2)p4g$ structure obtained are in good agreement with those obtained in earlier structural investigations, by other methods, including a full quantitative LEED study,[3] and are not discussed here further.

TABLE I. Structural parameter values for C on Ni(100) obtained from the full multiple scattering analysis of the PhD data. z values are interlayer distances perpendicular to the surface, the suffices C, 1 and 2 relating to the carbon and outermost and second Ni layers respectively; nn denotes only those atoms in the Ni layer closest to the C emitter. Δx is the radial displacement parallel to the surface of the Ni atoms closest to the isolated C adsorbate [cf. Fig. 1(a)]; Δxy is the magnitude of the displacement parallel to the surface of the outermost Ni atoms in the clock reconstruction. Values in italics are obtained from combinations of the primary parameters of the analysis, which define atoms positions relative to the C emitter. Δz values are layer rumpling amplitudes.

Parameter	Low-coverage phase (0.15 ML)	$(2 \times 2)p4g$ (0.50 ML)
z_{C1nn}	0.21 ± 0.07 Å	0.11 ± 0.04 Å
z_{C1}	0.19 ± 0.29 Å	
z_{C2nn}	1.95 ± 0.06 Å	1.94 ± 0.06 Å
z_{C2}	1.93 ± 0.30 Å	1.97 ± 0.12 Å
z_{12}	1.74 ± 0.10 Å	1.83 ± 0.07 Å
Δz_1	0.02 ± 0.20 Å	
Δz_2	0.02 ± 0.20 Å	
Δx	0.02 ± 0.02 Å	
Δxy		0.41 ± 0.07 Å

By contrast, the only prior study of the low coverage phase is the STM work referred to earlier.[6] The conclusions of this work were that the nearest-neighbor Ni atoms in the outermost atom layer were displaced radially outwards away from the C adsorbates by 0.15 ± 0.15 Å, and the layer spacing of these four Ni atoms around each C atom, relative to the second Ni layer, was reduced by ≈ 0.05 Å. Because of the influence of the C atom on the valence electrons in the vicinity of this adsorbate, both of these conclusions could be spurious, the observed image distortion being due to local electronic, rather than structural, modification. Notice that although the radial expansion of the hollow site given in the STM conclusions is formally not statistically significant (the error estimate is equal to the displacement value), this expansion *was* considered to be significant and was implicated in the origin of the C-C short-range repulsion evidenced in the STM images. Our results show that there is no significant radial expansion of the Ni atoms around the C adsorbate (the actual optimum value is 0.02 Å) to a much higher precision of ± 0.02 Å (a precision achieved through the inclusion of the strongly-modulated $\langle 100 \rangle$ grazing emission PhD spectra for which the role of these back scatterer atoms is dominant). On the other hand, our results do appear to support the slight outer-layer contraction of these near-neighbor Ni atoms, although in this case our own precision is not adequate to ensure that such contraction is statistically significant.

The formation of the clock reconstruction at higher carbon coverage causes the hollow sites on the surface to be enlarged, and in these larger ''cavities,'' the C atom is known to be almost coplanar with the outermost Ni layer. This has led to the idea that the driving force for the reconstruction is an attractive interaction of the C atom with the Ni atom directly below in the second layer; if the C atom can penetrate into the top layer it might be expected to shorten its distance from the second layer atom. We note, however, that the clock reconstruction is accompanied by an increase in the Ni outer layer spacing relative to the clean surface. This expansion can be understood qualitatively in a hard sphere picture as a consequence of the outer layer Ni atoms moving out of the hollow sites relative to the second layer. It is therefore interesting to calculate, from the atomic coordinates of Table I, the C-Ni near-neighbor distances in the low- and high-coverage structures. In the case of the low-coverage structure, the C atom lies in a simple undistorted hollow site relative to the top-layer nearest neighbors at a local layer spacing of 0.21 ± 0.07 Å, and the distance to these top-layer neighbors is thus 1.79 ± 0.02 Å, but the outermost Ni layer spacing is very close to that of the underlying bulk, so the distance of the C atom to the underlying second layer Ni atom is 1.95 ± 0.06 Å. In the clock-reconstructed phase the C-Ni outer-layer spacing is reduced to 0.11 ± 0.04 Å but there is a small expansion of the hollow site due to the top-layer lateral construction; nevertheless, the C-Ni nearest-neighbor distance to these outermost layer atoms is only 1.81 ± 0.02 Å, essentially the same as at low coverage. Moreover, the lower C-Ni outer-layer spacing is compensated by an expansion of the outermost Ni-Ni layer spacing, so even after including the effects of the small second-layer rumpling, the distance of the C atom to the underlying second layer Ni atom is 1.94 ± 0.06 Å. There are thus *no* significant differences in the near-neighbor C-Ni bonding dis-

tances in the surface before and after reconstruction, indicating that *neither* improved second-layer bonding *nor* nearest-neighbor surface layer Ni-C repulsion is the driving force.

It is striking that while the lateral displacement of the top-layer Ni atoms in the clock reconstruction is 0.41 Å, the increase in size of the hollow cavity is only 0.04 Å and, as we have seen, the C atom then falls to a lower spacing to conserve the Ni-C nearest-neighbor distance to within the experimental precision of 0.02 Å. By contrast, the Ni-Ni nearest-neighbor spacing for the outermost layer Ni atoms increases by 0.07 ± 0.02 to 2.56 Å. While small, this *increase*, associated with a phase transition that relieves increasing *compressive* stress[5]), is clearly highly significant relative to our precision, and is also a chemically significant bondlength change. It may be compared with the *reduction* [of 0.11 Å (Ref. 13)] in Au-Au surface atom spacing in the local symmetry conserving ''herringbone'' reconstruction of Au(111) driven by an intrinsic *tensile* stress. Moreover, this increase in Ni-Ni spacing is the only significant near-neighbor distance change associated with the reconstruction, suggesting that the true origin of the increasing C-induced compressive stress is Ni-Ni repulsion within the top layer. Notice that this implied C-induced Ni-Ni repulsion would lead to an effective (metal-mediated) C-C short-range repulsion on the Ni(100) surface as implied by the STM analysis of the adsorbate spacing.[6] Interestingly, earlier cluster calculations[14] led to the suggestion that the influence of the adsorbed C *was* to induce near-neighbor Ni-Ni repulsion, leading to the compressive stress; our own determination of the change in local geometry confirms this view and suggests that it is this Ni-Ni repulsion, which is the driving force for the reconstruction.

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